

CONDUCTIVE FINE PARTICLE AND ANISOTROPIC CONDUCTIVE MATERIAL

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Abstract of JP2004111163

PROBLEM TO BE SOLVED: To provide a conductive fine particle having a good corrosion resistance and stability with time of a metal coating layer, and an anisotropic conductive material using above.

SOLUTION: The resin fine particle is directly covered with a metal conductive layer made of gold having a purity of not less than 95 wt.%.

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(54) 【発明の名称】 導電性微粒子及び異方性導電材料

(57) 【要約】

【目的】 本発明は金属被覆層の耐腐食性、経時安定性に優れた導電性微粒子、ならびにそれを用いた異方性導電材料を提供することを目的とする。

【構成】 純度が95重量%以上の金からなる金属導電層で樹脂微粒子を直接被覆する

【特許請求の範囲】

【請求項 1】

樹脂微粒子の表面に金属被覆層が直接形成されてなる導電性微粒子であって、金属被覆層の 95 重量%以上が金から成ることを特徴とする導電性微粒子。

【請求項 2】

該金属被覆層に含有される Ni が 5 重量%未満であることを特徴とする請求項 1 に記載の導電性微粒子。

【請求項 3】

樹脂微粒子の表面に金属被覆層が形成されてなる導電性微粒子であって、該樹脂微粒子に水素吸蔵能のある金属を吸着させた後、無電解金メッキにより金属被覆層を形成してなる 10
り、該金属被覆層の 95 重量%以上が金からなることを特徴とする導電性微粒子。

【請求項 4】

樹脂微粒子の表面に金属被覆層が形成されてなる導電性微粒子であって、該樹脂微粒子に無電解ニッケルメッキによる金属被覆層を設けた後、置換金メッキではほぼ完全にニッケルを金に置換して金属被覆層を形成してなり、該金属被覆層の 95 重量%以上が金からなり、ニッケルが 5 重量%未満であることを特徴とする導電性微粒子。

【請求項 5】

置換金メッキ後、さらに無電解金メッキにより金属被覆層を形成してなる導電性微粒子であって、該金属被覆層の 95 重量%以上が金であり、ニッケルが 5 重量%未満であることを特徴とする請求項 4 に記載の導電性微粒子。 20

【請求項 6】

樹脂微粒子の平均粒径が $1 \sim 20 \mu\text{m}$ であり、かつ変動係数が 10 % 以下であって、金属被覆層の厚みが $0.005 \sim 1 \mu\text{m}$ であることを特徴とする請求項 1～5 に記載の導電性微粒子。

【請求項 7】

請求項 1～6 のいずれか 1 項に記載の導電性微粒子が用いられて成ることを特徴とする異方性導電材料。

【発明の詳細な説明】

【産業上の利用分野】

本発明は金属被覆層の耐腐食性、経時安定性に優れた導電性微粒子、ならびにそれを用いた異方性導電材料に関する。 30

【0001】

【従来の技術】

導電性微粒子は、バインダー樹脂等と混合させるなどして、異方導電性フィルム、導電性ペースト、導電性接着剤、導電性粘着材等の異方性導電材料の主要構成材料として広く用いられている。これらの導電材料は液晶表示ディスプレイ、パーソナルコンピュータ、携帯電話等の電子機器において、基板同士を電気的に接続したり、半導体素子等の小型部品を基板に電気的に接着したりするために、相対向する基板や電極端子の間に挟み込んで使用されている。

【0002】

この導電性微粒子としては、従来より、金、銀、ニッケル（以下 Ni と表す）等の金属粒子が用いられてきたが、比重が大きく形状も不定形であるため基板同士を一定の間隔で保持することが困難であったり、バインダー樹脂中で不均一に存在しやすく、導電性にムラを生じさせたりする問題が生じ、日々ファインピッチ化の進む電子部品には使用が困難となってきた。

また、硬度が高く弾力性に乏しかったため基板に損傷を与え、さらにはバインダー樹脂との熱膨張率の違いが大きいため温度の急激な変化等により接続部にクラックを生じることがあり、長期の使用においては経時的に導通性の不良を来す場合があった。

【0003】

このため近年では金属粒子の代わりに粒径が均一で、適度な強度を有するプラスチックボ 50

ールなどの非導電性粒子の表面に無電解Niメッキを施した導電性微粒子が広く用いられてきている。しかしながらNiは接触抵抗が高く、高温高湿下に長時間さらされると変質し、接触導通性を更に悪化させるという欠点があった。

【0004】

このような問題を解決するために、例えば特開平7-118866号公報には球状粒子の表面に無電解Niメッキを施し、さらにその上層に置換金メッキ層を形成させた導電性微粒子が開示されている。しかしながら、下地のNi層は容易に酸化被膜を作りやすく、この影響のため金被覆を均一にすることが一般的には困難であった。さらには、微小なピンホールやNiの部分露出が存在すると、いわゆる“局部電池”を生じて下地Niの溶出を加速させ、溶出したNiは金属被覆層の表面に酸化物として析出し接触導通性を著しく低下させてしまうという問題点があった。また、変質した金属被覆層はメッキ割れやはがれを生じやすくなり、ちょっとした衝撃や振動によってもメッキ層にクラックを生じ、このような金属メッキ層の腐食やメッキ割れは導電材料として使用した場合に導通性不良をきたすばかりではなく、経時的に腐食が進行することにより導電材料の信頼性を著しく低下させる原因となり得た。

【0005】

一方、特開平9-171714号公報には樹脂粒子の表面に乾式コーティング法で金を付着させ、さらに無電解金メッキで金を被覆する方法が開示されている。しかしながら、乾式コーティングで微粒子に金をまんべんなく付着させることは困難であるため、近年の電子機器の急激な進歩に伴う更なる経時安定性の要求に対しては未だ十分満足させるものではなかった。

【0006】

【発明が解決しようとする課題】

本発明は、上記問題点を解決するものであり、その目的とするところは、導電被覆層である金属被覆層が均一で耐腐食性が高く、経時安定性の優れた導電性微粒子を提供することにある。さらには、該導電性粒子を使用することにより、長期間の使用においても金属メッキ層の腐食やメッキ割れによる導電性低下を来さない経時安定性の高い異方性導電材料を提供することにある。

【0007】

【課題を解決するための手段】

本発明者らは鋭意検討した結果、純度が95重量%以上の金からなる金属導電層で樹脂微粒子を被覆した導電性微粒子は耐腐食性が著しく高く、かつ、局部電池を生じることもなく経時安定性が著しく向上することを見出し、本発明を完成させるに至った。

【0008】

本発明の導電性微粒子は、樹脂微粒子の表面に金属被覆層が直接形成されてなる導電性微粒子であって、金属被覆層の95重量%以上が金から成ることを特徴とするものである。導電性微粒子。さらには、樹脂微粒子に水素吸蔵能のある金属を吸着させた後、無電解金メッキにより金属被覆層を形成してなる導電性微粒子であって、該金属被覆層の95重量%以上が金からなることを特徴とするもの、また、樹脂微粒子に無電解ニッケルメッキによる金属被覆層を設けた後、置換金メッキではほぼ完全にニッケルを金に置換することにより金属被覆層を形成してなる導電性微粒子であって、金属被覆層の95重量%以上が金であり、Niが5重量%未満であることを特徴とするもの、及び、さらに無電解金メッキにより金属被覆層を形成してなる導電性微粒子であって、該金属被覆層の95重量%以上が金であり、Niが5重量%未満であることを特徴とするものであり、これらは樹脂微粒子の表面上に耐腐食性が高く均一な金属被覆層を形成しており、局部電池を生じることもなく経時安定性に優れたものであるという結果をもとに構成されている。

【0009】

以下に本発明を詳説する。

本発明の樹脂微粒子としては、種々の有機物が好適であり、ポリエチレン、ポリプロピレン、ポリスチレン、ポリ塩化ビニル、ポリ塩化ビニリデン、ポリプロピレン、ポリイソブ

チレン、ポリブタジエン等のポリオレフィン、ポリメチルメタクリレート、ポリメチルアクリレート等のアクリル樹脂、ポリアルキレンテレフタレート、ポリスルホン、ポリカーボネート、ポリアミド、フェノールホルムアルデヒド樹脂、メラミンホルムアルデヒド樹脂、ベンゾグアナミンホルムアルデヒド樹脂、尿素ホルムアルデヒド樹脂等が用いられる。例えば、エチレン性不飽和基を有する種々の重合性単量体を1種もしくは2種以上重合させることにより、導電材料に適した任意の圧縮時の物性を有する樹脂微粒子を設計・合成することができる。

【0010】

該樹脂微粒子を、エチレン性不飽和基を有する重合性単量体を重合させて得る場合、上記エチレン性不飽和基を有する単量体としては、非架橋性の単量体と架橋性の単量体があり 10、非架橋性の単量体としては、例えば、スチレン、 α -メチルスチレン等のスチレン系単量体、(メタ)アクリル酸、マレイン酸、無水マレイン酸等のカルボキシル基含有単量体、メチル(メタ)アクリレート、エチル(メタ)アクリレート、プロピル(メタ)アクリレート、ブチル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート、ラウリル(メタ)アクリレート、セチル(メタ)アクリレート、ステアリル(メタ)アクリレート、シクロヘキシル(メタ)アクリレート、イソボルニル(メタ)アクリレート等のアルキル(メタ)アクリレート類、2-ヒドロキシエチル(メタ)アクリレート、グリセロール(メタ)アクリレート、ポリオキシエチレン(メタ)アクリレート、グリシジル(メタ)アクリレート等の酸素原子含有(メタ)アクリレート類、(メタ)アクリロニトリル等のニトリル含有単量体、メチルビニルエーテル、エチルビニルエーテル、プロピルビ 20ニルエーテル等のビニルエーテル類、酢酸ビニル、酪酸ビニル、ラウリン酸ビニル、ステアリン酸ビニル等の酸ビニルエステル類、エチレン、プロピレン、イソブレン、ブタジエン等の不飽和炭化水素、及びトリフルオロメチル(メタ)アクリレート、ペンタフルオロエチル(メタ)アクリレート、塩化ビニル、フッ化ビニル、クロルスチレン等のそれらのハロゲン含有単量体等が挙げられる。

【0011】

また、架橋性の単量体としては、例えば、テトラメチロールメタンテトラ(メタ)アクリレート、テトラメチロールメタントリ(メタ)アクリレート、テトラメチロールメタンジ(メタ)アクリレート、トリメチロールプロパントリ(メタ)アクリレート、ジペンタエリスリトールヘキサ(メタ)アクリレート、ジペンタエリスリトールペンタ(メタ)ア 30クリレート、グリセロールトリ(メタ)アクリレート、及びグリセロールジ(メタ)アクリレート、ポリエチレングリコールジ(メタ)アクリレート、ポリプロピレングリコールジ(メタ)アクリレート等の多官能(メタ)アクリレート類、トリアリル(イソ)シアヌレート、トリアリルトリメリテート、および、ジビニルベンゼン、ジアリルフタレート、ジアリルアクリルアミド、ジアリルエーテル等、 γ -(メタ)アクリロキシプロピルトリメトキシシラン、トリメトキシシリルスチレン、ビニルトリメトキシシラン等のシラン含有単量体等が挙げられる。

【0012】

上述のエチレン性不飽和基を有する重合性単量体を、公知の方法、例えば、ラジカル重合開始剤の存在下、懸濁重合する方法(特開平6-273774号公報)、非架橋の種粒子 40にラジカル重合開始剤とともに単量体を膨潤させて重合する方法(特開平1-81810号公報)等により重合することにより、本発明の樹脂微粒子を得ることができる。

【0013】

これらの樹脂微粒子は特に限定されるものではなく、単独で用いられても、2種以上を併用してもよいが、導電材料として用いられるためには樹脂微粒子の圧縮時の物性が重要視される。

【0014】

例えば、機械的強度の指標として用いられる10%K値が1000~15000MPaであるものが好ましく、さらには2000~10000MPaであるのがより好ましい。

【0015】

10%K値とは、特表平6-503180号公報に準拠して微小圧縮試験器（島津製作所製PCT-200）を用い、得られた樹脂微粒子を直径50μmのダイヤモンド製円柱からなる平滑圧子端面で、圧縮速度0.27g/秒、最大試験過重10gの条件下で圧縮することにより測定され、下記の式より10%K値を求めることが出来る。

$$K = (3/\sqrt{2}) \cdot F \cdot S^{-3/2} \cdot R^{-1/2}$$

F：粒子の10%圧縮変形における荷重値（kg）

S：粒子の10%圧縮変形における圧縮変位（mm）

R：粒子の半径（mm）

【0016】

上記10%K値が1000未満では、樹脂微粒子の強度が十分でないため、圧縮変形させたとき粒子の破壊が生じ、導電材料としての機能を果たさなくなる。逆に15000より大きいと電極を傷つけることがあるので好ましくない。

【0017】

さらに、本発明の樹脂微粒子は、回復率が20%以上であることが好ましい。回復率とは粒子に1gfの荷重を負荷した後の回復率であり、より好ましくは40%以上である。回復率が20%未満である樹脂微粒子を用いて導電性微粒子を製造すると、圧縮した場合に変形しても元に戻らないため接続不良を起こすことがある。

【0018】

本発明に使用される樹脂微粒子を、前述のエチレン性不飽和基を有する重合性単量体を重合させて得る場合、これらの粒子物性を考えると樹脂微粒子中の構成成分として、架橋性単量体を少なくとも5重量%以上、より好ましくは20重量%以上含有することがより好ましい。架橋性単量体が5重量%未満であると、上記10%K値や回復率が低下し、圧着処理を行った際、導電性微粒子の破壊や永久変形を生じ好ましくない。

【0019】

本発明の導電性微粒子は純度が95重量%以上の金からなる金属被覆層を上記の樹脂微粒子の表面に直接形成することにより得られる。この場合、樹脂微粒子に直接形成することとは、純度が95重量%以上の金からなる金属被覆層と樹脂微粒子との間に無電解Ni等による下地層が存在しないことを意味する。また該金属被覆層は均一に樹脂微粒子を覆いつくしていることが望ましいが、導電性やメッキ剥離に影響のない程度のピンホールや被覆ムラがあっても別段差し支えない。なぜなら微小なピンホールや僅かな被覆ムラがあったとしても、局部電池の基点となるべき下地ニッケル層が充分に存在しないので金属導電層の腐食や経時的な変質を起こさない。

【0020】

該金属被覆層の形成方法としては以下に挙げる方法が好適である。

1. 樹脂微粒子に水素吸蔵能のある金属を吸着させた後、無電解メッキにより金を樹脂微粒子の表面に直接形成する方法

2. 樹脂微粒子の表面に無電解Niメッキ層を施し、その後、金によりほぼ完全に置換する方法

3. 2で製した金属被覆層にさらに電気メッキもしくは無電解メッキにより金被覆層の膜厚を増加させる方法。

【0021】

1の方法としては、種々の市販されている自己還元型の無電解金メッキ試薬も使用でき、特に限定されないが、一般的にエッチング工程、触媒化工程、無電解メッキ工程から成り立っている。

【0022】

エッチング工程はクロム酸、硫酸-クロム酸混液、過マンガン酸溶液等の酸化剤や、塩酸、硫酸等の強酸、水酸化ナトリウム、水酸化カリウム等の強アルカリ溶液等を用いて基材微粒子の表面に微小な凹凸を形成させ、これによってメッキ層の密着を良くするための工程である。

【0023】

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触媒化工程は樹脂微粒子の表面に次工程の無電解メッキの起点となりうる水素吸蔵能を有する金属を樹脂微粒子に吸着生成させることによってなる触媒層を形成させる工程である。ここで水素吸蔵能のある金属としては特に限定されないが、Pd, Pt, Au, Ni等が挙げられるが、市販の試薬等が広く出回っているPdを用いることが最も簡便であり好ましい。Pdを用いる触媒化工程としては、特に限定されるものではなく、市販のPd触媒化液等を用いる場合の他、例えば、塩化パラジウムと塩化スズからなる溶液に、エッチングした樹脂微粒子を浸漬したのち、硫酸、塩酸等の酸、水酸化ナトリウム等のアルカリ溶液で活性化してPdを樹脂微粒子表面に析出させる方法、硫酸パラジウム溶液にエッチングした樹脂微粒子を浸漬したのち、ジメチルアミンボラン等の還元剤を含む溶液で活性化してPdを樹脂微粒子表面に析出させる方法等が挙げられる。しかしながら前者はスズや塩化物が金属被膜中に残存する場合が多く後者の方法の方がより好ましい。

【0024】

無電解メッキ工程は触媒を付与した樹脂微粒子を、還元剤の存在下で金を含有する溶液中に浸漬し、付与された触媒を起点として樹脂微粒子の表面に金を析出させることにより行われる。

【0025】

この場合使用される還元剤としては特に限定されるものではなく、テトラヒドロホウ酸塩、シアノテトラヒドロホウ酸塩、ジメチルアミンボラン、ヒドラジンボラン等のホウ素化合物、次亜リン酸塩、ヒドラジン、ブドウ糖、ホルマリン、アスコルビン酸、三塩化チタン等を用いることが出来る。また、金を溶液中に含有させる方法としては通常シアン化金塩、ニシアン化金塩、四塩化金塩等の金含有水溶性塩を用いることが好適である。

【0026】

これらの還元剤と金含有水溶性塩をクエン酸塩、エチレンジアミン四酢酸塩等のキレート剤、シアン化カリウム、シアン化ナトリウム、トリエタノールアミン、エチレングリコールモノエチルエーテル、ジエチレングリコールモノエチルエーテル、ポリエチレンジアミン、酢酸鉛等の添加剤や安定剤と共に溶解し自己還元型無電解金メッキ浴を建浴することができ、これらのメッキ浴を用いて金被覆層は樹脂微粒子の表面に直接形成することが出来る。

【0027】

本発明の金属被覆層は金が主成分となるが、金と共に共析する他の金属が含まれていてもよく、例えばCo, Cu, Zn, Fe, Mn, Cr, V, Mo, Pd, Sn, Ni等が金と共に導電被覆層に含まれていても良いが、金の純度は95W/W%以上であることが好ましく、より好ましくは98W/W%以上である。金の純度が95W/W%以下であると接触導電性や金属皮膜の柔軟性が低下し好ましくない。

【0028】

1の方法では、金属被覆層の膜厚は置換金メッキの試薬量、時間、温度等で任意に制御することが出来る。

【0029】

2の方法は、一旦無電解ニッケルメッキにより、Ni金属層を形成し、これを置換金メッキ浴に投入しほぼ完全にNiを金と置換せしめる方法であり、特に限定されないが、同様にエッチング工程、触媒化工程、無電解Niメッキ工程、置換金メッキ工程から成り立っている。エッチング工程および触媒化工程は1の方法と同様であり、無電解Niメッキ工程についても種々の市販されている無電解Niメッキ浴を使用することができるが、例えば、触媒を付与した樹脂微粒子を、次亜リン酸、ジメチルアミンボラン等の還元剤の存在下でニッケル塩を含有する溶液中に浸漬し、付与された触媒を起点として樹脂微粒子の表面にニッケルを析出させることにより行われる。置換金メッキ工程はNiと金とのイオン化傾向の違いを利用して、Niと金と置換する工程であり、種々の市販されている置換金メッキ浴が使用できるが、例えばクエン酸塩、エチレンジアミン四酢酸塩等のキレート剤、シアン化金塩、ニシアン化金塩、四塩化金塩等の金含有水溶性塩を溶解して建浴することができる。通常この置換金メッキ浴には還元剤は含まれていない。

【0030】

2の方法は1の方法で用いた無電解金メッキ浴よりも安定である無電解Niメッキ浴を使用できるという利点があるが、置換金メッキ工程においてほぼ完全にNiを金と置換させる必要がある。この場合のほぼ完全とは、金の置換率が金属被覆層中の金純度として95重量%以上であることが好ましく、より好ましくは98重量%以上である。金の純度が95重量%以下であると接触導電性や金属皮膜の柔軟性が低下し好ましくない。

【0031】

また、残存するNiが5重量%未満であることが好ましく、Niが2重量%以下となるまで金で置換することがより好ましい。Niの残存率が5重量%以上であると、微小なピンホールや被覆ムラを起点として局部電池を生じ易くなり好ましくない。

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【0032】

2の方法では金属被覆層の厚みは無電解Ni層の厚みに依存するが、金の置換率を上げるために無電解Niメッキ層をあまり厚くすべきではなく、2の方法では無電解Niメッキ層は0.04 μ m以下であることが望ましく、0.02 μ m以下であることがより好ましい。Niメッキ層が0.04 μ mを超えると95重量%以上の金置換が困難になる。このような理由で2の方法では金メッキ層をあまり厚くすることができず、更に金被覆層の厚みを増加させるためには3の方法を用いることがより好ましい。

【0033】

3の方法では無電解Niメッキ層を2の方法よりも予め薄く設定できるので、Niの残存率をより低くすることが可能となる。3の方法で用いる無電解金メッキの方法は1の方法と同様にしてなされる。最終的に得られた金属被覆層中の金の含量は95重量%以上であることが好ましく、より好ましくは98重量%以上である。金の純度が95重量%以下であると接触導電性や金属皮膜の柔軟性が低下し好ましくない。

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また、残存するNiが5重量%未満であることが好ましく、Niが2重量%以下となるまで金で置換することがより好ましい。Niの残存率が5重量%以上であると、微小なピンホールや被覆ムラを起点として局部電池を生じ易くなり好ましくない。

【0034】

該金属被覆層の厚みとしては被覆する樹脂微粒子の平均粒子径によっても異なるが、0.005~1 μ mであることが好ましく、更には0.01~0.3 μ mであることがより好ましい。該被覆層の厚みが0.005 μ m未満であると導電被覆層としての十分な効果が得られず好ましくない。また、該被覆層が1 μ mを超えると粒子比重が大きくなりすぎたり、高価な金を多量に必要としコスト高となるのであまり好ましくない。

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【0035】

本発明の樹脂微粒子は平均粒径が0.5~100 μ mであるものが好ましく、1~20 μ mの範囲であるものがより好ましい。樹脂微粒子が0.5 μ m未満であると、導電性被覆層を形成する際に凝集が生じやすく、この粒子を用いて製造される導電性微粒子は隣接電極間のショートを引き起こすという問題を発生することがある。樹脂微粒子の平均粒径が100 μ mを超えると、この粒子を用いて製造される導電性微粒子の導電性被覆層が剥がれ易くなり信頼性が低下するという問題が発生することがある。

【0036】

また、粒子径分布から得られる標準偏差を平均粒径で除して得られる変動係数が10%以下であるものがより好ましい。また、変動係数が10%を超える樹脂微粒子を用いて導電性微粒子を製造すると、相対向する電極間隔を任意に制御することが困難になる。

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【0037】

本発明の導電性微粒子は、種々の異方性導電材料の主要構成材料として使用され、相対向する2つの基板や電極端子を電気的に接続する際に用いられ、本発明の導電性微粒子を含有する異方性導電材料も本発明に含まれる。その方法としては特に限定されず、例えば、導電性微粒子をバインダー樹脂中に分散させて異方性導電接着剤とし、この異方性導電接着剤を使用して接続する方法、バインダーと導電性微粒子とを別々に使用して接続する方法等が挙げられる。

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【0038】

上記異方性導電接着剤としては、導電性微粒子を絶縁性のバインダー樹脂中に分散させたものであれば特に限定されず、異方性導電膜、異方性導電ペースト、異方性導電インク等を含むものである。

【0039】

該バインダー樹脂としては特に限定されず、例えば、アクリレート樹脂、エチレン-酢酸ビニル樹脂、スチレン-ブタジエンブロック共重合体等の熱可塑性樹脂、グリシジル基を有するモノマーやオリゴマー及びイソシアネート等の硬化剤との反応により得られる硬化性樹脂組成物等の光や熱によって硬化する組成物等が挙げられる。上記異方性導電材料の塗工膜厚は、使用した導電性微粒子の平均粒径と接続電極の仕様から計算し、接続電極間に導電性微粒子が挟持され、接合基板間が接着層で十分に満たされるようにすることが好ましい。

【0040】

異方性導電膜は、例えば、上記異方性導電接着剤に溶媒を加えて溶液状とし、この溶液を離型フィルム上に流延して被膜を作り、皮膜から溶媒を蒸発させたものをロール上に巻き取って作ることができる。使用の際には皮膜を離型フィルムと共に巻き出して、皮膜を接着すべき電極上に置き、この上に対向電極を重ねて加熱圧縮することにより接続させることができる。

【0041】

異方性導電ペーストは、例えば、異方性導電接着剤をペースト状にすることにより得られ、これを適当なディスペンサーに入れ、接続すべき電極上に所望の厚みに塗り、この上に対向電極を重ね合わせ、加熱するとともに加圧して樹脂を硬化させることにより、接続させることができる。

【0042】

異方性導電インクは、例えば、上記異方性導電接着剤に溶媒を加えて印刷に適した粘度を持たせることにより得ることができ、これを接着すべき電極上にスクリーン印刷し、その後溶媒を蒸発させ、この上に対向電極を重ねて加熱圧縮することにより接続させることができる。

【0043】

【作用】

本発明により得られる導電性微粒子は、導電被覆層である金属被覆層が均一で耐腐食性の良好な、経時安定性の優れた導電性微粒子を得ることができる。さらには、該導電性粒子を使用することにより、長期間の使用においても金属メッキ層の腐食やメッキ割れによる導電性低下を来さない経時安定性の高い異方性導電材料を得ることができる。

【0044】

(実施例)

以下に実施例を上げて本発明を更に詳しく説明するが、本発明はこれら実施例のみに限定されるものではない。

【0045】

(実施例1)

ポリビニルアルコール（日本合成化学工業製 GH-20）の3%水溶液800部（以下重量部）に、ジビニルベンゼン80部、トリメチロールプロパントリ（メタ）アクリレート20部、過酸化ベンゾイル2部の混合液を加えてホモナイザーにて攪拌して粒度調整を行った。その後攪拌しながら窒素気流下にて80℃まで昇温し、15時間反応を行った。得られた微粒子を蒸留水及びメタノールにて洗浄後分級操作を行い、平均粒径=5.3 μm 、変動係数5.0%の芯材となる樹脂微粒子を得た。この樹脂微粒子の10%K値を前述の方法により測定したところ4100MPa、回復率が51%であった。この樹脂微粒子10gを粉末メッキ用プレディップ液（奥野製薬社製）に分散させ、30℃で30分間攪拌することによりエッチングした。

【0046】

その後、該微粒子を水洗して、硫酸パラジウムを1重量%含有するPd触媒化液100mlに添加し、30℃で30分間攪拌させてパラジウムイオンを粒子に吸着させた。この粒子を濾取、水洗した後、0.5重量%のジメチルアミンボラン液(pH6.0に調整)に添加し、Pdを活性化させた樹脂微粒子を得た。

【0047】

該樹脂微粒子にニシアン化金カリウムを7g/L含有する還元型無電解金メッキ液100ml(セラゴールド6020、EEJA製)を加え、超音波洗浄機を用いて十分に分散させたあと、攪拌しながら70℃まで昇温させた時点で10%水溶液を徐々に添加しながら無電解金メッキを実施した。金被覆層がおおよそ0.04μmになった時点で反応を止め、粒子を濾取した。この粒子を蒸留水で十分に水洗したのちアルコール置換し真空乾燥させて導電性微粒子1を得た。この導電性微粒子1を電子顕微鏡(SEM)を用いて5000倍にて観察したところメッキ欠損等のない均一な金属被覆層が形成されていることが確認できた。

また、得られた導電性微粒子1について以下に挙げる金属被覆層の厚み測定、金属含有比率測定、導電性と導電被覆層の密着性の測定、高温高湿負荷後の導電性等変化の測定を実施し、その結果を表1に示した。

【0048】

(金属被覆層の厚み測定)

導電性微粒子1を0.5g精秤し、60%硝酸5mlと37%塩酸10mlからなる混合液に加え金属被覆層を完全に溶解させたあと、硫酸ヒドラジンの飽和水溶液20mlを加えて80℃にて1時間加熱し金を沈殿させた。この沈殿した金を含む溶液を濾紙で濾取し、濾紙のままルツボに入れ900度で2時間焼却して金を回収した。回収された金の重量を測定し金含有率(WAUと言う)を算出した。得られた金含有率より下記式にて金のメッキ層厚を算出した。

$$\text{金メッキ層厚}(\mu\text{m}) = (\rho_P \times \text{WAU} \times D) / \{6 \times \rho_{AU} \times (100 - \text{WAU})\}$$

ρ_P :樹脂微粒子の比重、 ρ_{AU} :金の比重、WAU:金含有率(%）、D:樹脂微粒子の平均粒径(μm)

【0049】

(金属被覆層の金属含有比率測定)

上記の金属被覆層の厚み測定と同様にして金属被覆層を完全に溶解した溶液をICP発光分析計にて測定し、金及びNi等その他に含有される金属の重量%を算出した。

【0050】

(導電性と導電被覆層の密着性の測定)

微小圧縮電気抵抗測定器(PCT-200改、島津製作所社製)を用いて導電性微粒子1を圧縮し、粒径の20%圧縮された時点での接触抵抗値を測定した。この測定を粒子20個に対して実施し、その平均値を求めた。

【0051】

また、引き続き平均粒径の50%まで徐々に圧縮していくと、その過程において突然抵抗値が10Ω以上に増大する粒子が認められた。これらの粒子を光学顕微鏡にて観察すると、導電被覆層の剥離、破壊が発生しており、これらの粒子の発生比率を導電性破壊比率として求めた。この導電性破壊比率が低いほどメッキ割れが少ないことを示す。

【0052】

(高温高湿負荷後の導電性等変化の測定)

導電性微粒子1を85℃、相対湿度95%の雰囲気下で20日間放置したのち、上記導電性の測定と同様にして負荷後の接触抵抗値と導電性破壊比率を求めた。負荷前後の測定値の差が小さいほど、経時安定性に優れた導電性微粒子であることを示す。

【0053】

(実施例2)

実施例1と同様にして得られた、Pdを活性化させた樹脂微粒子に蒸留水500mlを加

え、超音波処理機を用いて十分に分散させることにより微粒子懸濁液を得た。この懸濁液を50℃で攪拌しながら、硫酸ニッケル(6水和物)50g/L、ジメチルアミンボラン5g/L、クエン酸50g/Lからなる無電解メッキ液(pHは7.5に調整)を徐々に添加し無電解ニッケルメッキを行った。該被覆層が約0.02μmになった時点で無電解メッキ液の添加をやめ、粒子を濾取した。この粒子を蒸留水で十分に水洗したのち、ニシアン化金カリウム7gを含有する置換金メッキ液(日本高純度化学社製、IM-GoldST)2000mlに添加して、攪拌しながら70℃にて60分反応させ、Niメッキ層を完全に金にて置換した。反応終了後に微粒子を濾取、水洗し、アルコール置換したのち真空乾燥させ導電性微粒子2を得た。

【0054】

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この導電性微粒子2を実施例1と同様にSEMにて観察したところメッキ欠損等のない均一な金属被覆層が形成されていることが確認できた。導電性微粒子2を実施例1と同様にして、金属被覆層の厚み測定、金属含有比率測定、導電性と導電被覆層の密着性の測定、高温高湿負荷後の導電性等変化の測定を実施し、その結果を表1に示した。

【0055】

(実施例3)

実施例2と同様にして無電解ニッケルメッキを行い、該Ni被覆層が約0.01μmになった時点で無電解メッキ液の添加をやめ、粒子を濾取した。この粒子を実施例2と同様にして、Niメッキ層を完全に金にて置換した。得られた粒子を再度実施例1と同様にして自己還元型無電解金メッキを行い、反応終了後に微粒子を濾取、水洗し、アルコール置換したのち真空乾燥させ導電性微粒子3を得た。この導電性微粒子3を実施例1と同様にSEMにて観察したところメッキ欠損等のない均一な金属被覆層が形成されていることが確認できた。

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【0056】

導電性微粒子3を実施例1と同様にして、金属被覆層の厚み測定、金属含有比率測定、導電性と導電被覆層の密着性の測定、高温高湿負荷後の導電性等変化の測定を実施し、その結果を表1に示した。

【0057】

(比較例1)

実施例2と同様にして無電解ニッケルメッキを行い、該Ni被覆層が約0.05μmになった時点で無電解メッキ液の添加をやめ、粒子を濾取した。この粒子を蒸留水で十分に水洗したのち、シアン化金カリウム5gを含有する置換金メッキ液(日本高純度化学社製、IM-GoldST)2000mlに添加して、攪拌しながら70℃にて反応させ、置換金メッキ層の厚みが約400Åになる時点で反応を中止した。その後微粒子を濾取、水洗し、アルコール置換したのち真空乾燥させ導電性微粒子4を得た。

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【0058】

導電性微粒子4についても実施例1と同様にして、導電性と導電被覆層の密着性の測定、高温高湿負荷後の導電性等変化の測定を実施し、その結果を表1に示した。

【0059】

(比較例2)

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実施例2において、置換金メッキの反応時間を60分から10分に減らして金への置換率を不十分にしたこと以外は同様に行い導電性微粒子5を得た。得られた導電性微粒子5についても実施例1と同様にして、導電性と導電被覆層の密着性の測定、高温高湿負荷後の導電性等変化の測定を実施し、その結果を表1に示した。

【0060】

なお、導電性微粒子4及び5の金及びNi膜厚は以下の方法により測定した。(金及びNi膜厚の測定)

導電性微粒子0.5gを精秤し、60%硝酸5mlと37%塩酸10mlからなる混合液に加え金属被覆層を完全に溶解させたあと、硫酸ヒドラジンの飽和水溶液20mlを加えて80℃にて1時間加熱し金を沈殿させた。この沈殿した金を含む溶液を濾紙で濾取し、

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濾紙のままルツボに入れ900度で2時間焼却して金を回収した。回収された金の重量を測定し金含有率WAUを算出した。また濾液は正確に200mlにメスアップし、弱酸性下Cu-PANを指示薬として0.01mol/LのEDTA標準液にてニッケル含有率(WNiと言う)を測定した。

【0061】

得られた金含有率及びニッケル含有率より下記式にて金、ニッケルのメッキ層厚を算出した。

金メッキ層厚(μm) = $(\rho P \times WAU \times D) / \{6 \times \rho AU \times (100 - WAU - WNi)\}$

Niメッキ層厚(μm) = $(\rho P \times WNi \times D) / \{6 \times \rho Ni \times (100 - WAU - WNi)\}$ 10

ρP:樹脂微粒子の比重、ρAU:金の比重 ρNi:Ni層の比重、
WAU:金含有率(%)、WNi:ニッケル含有率(%)、D:樹脂微粒子の平均粒径(μm)

【0062】

表1より、実施例1~3で得られた導電性微粒子1~3は比較例1及び2で得られた導電性微粒子4及び5に比べて負荷後の導電性変化やメッキ割れの増加が少なく金属被覆層の耐腐食性が高いことがわかる。負荷後の導電性微粒子4は他の導電性微粒子と比べて暗色化しており、それぞれの負荷前後の導電性微粒子を電子顕微鏡(SEM)を用いて5000倍にて観察したところ、導電性微粒子1~3ではその表面性に大きな変化は認められなかったが、比較例の導電性微粒子4及び5では蜘蛛の巣状の表面変質が認められた。これは希塩酸に容易に溶解し、この溶液からNiが検出されたことから、この表面変質は局部電池が発生する等の影響で下層のNiが溶出し、導電性微粒子の表面にNi酸化物等となって付着したものと考えられる。 20

【0063】

(実施例4)

導電性微粒子1をエポキシ系接着剤(古川化工社製、SE-4500)に5W/W%の割合で混合し、ホモジナイザーで十分に分散させて異方性導電接着剤1を作製した。

【0064】

この異方性導電接着剤を幅300μmでITO電極が形成されたガラス基板上にそれぞれ塗布し、この上から同じガラス基板をITO電極がクロスになるよう重ね合わせた。これに30kg/cm²の圧力を加えながら160℃で30分間加熱して圧着硬化させたのち、ITOが交差する部分に存在する導電性微粒子1について4端子法により接触抵抗値の測定を行った。交差する部分に存在する導電性微粒子1の数を光学顕微鏡にて計数し、得られた接触抵抗値をこの数で除して、導電性微粒子1個当たりの接触抵抗値とした。 30

【0065】

さらにこの基板を85℃、相対湿度95%の雰囲気下で20日間放置したのち、再度同様の測定を実施した。この測定をそれぞれn=5実施し、平均値を表2に示した。この接触抵抗値の変化が小さいほど導電性の経時安定性が良好であることを示す。 40

【0066】

(実施例5)

導電性微粒子2を用いたこと以外は実施例4と同様の操作を行い異方性導電接着剤2を作製し、実施例4と同様の測定を実施した。得られた結果を表2に示した。

(実施例6)

導電性微粒子3を用いたこと以外は実施例4と同様の操作を行い異方性導電接着剤3を作製し、実施例4と同様の測定を実施した。得られた結果を表2に示した。

【0067】

(比較例3)

導電性微粒子4を用いたこと以外は実施例4と同様の操作を行い異方性導電接着剤4を作製し、実施例4と同様の測定を実施した。得られた結果を表2に示した。 50

【0068】

(比較例4)

導電性微粒子5を用いたこと以外は実施例4と同様の操作を行い異方性導電接着剤5を作製し、実施例4と同様の測定を実施した。得られた結果を表2に示した。

【0069】

表2より、実施例4～6で製した異方性導電接着剤1～3は比較例3、4の異方性導電接着剤4及び5よりも経時安定性が優れていることがわかる。

【0070】

【表1】

	導電性 微粒子	Au厚 (μm)	Ni厚 (μm)	被覆層の金属含有比 率(%)			接 触 抵 抗 (Ω)		導電性破壊比 率(%)	
				Au	Ni	その他 (Pd)	初期	負荷後	初期	負荷後
実施例1	1	0.040	—	99.7	0.0	0.3	1.2	1.3	0	0
実施例2	2	0.040	—	98.1	1.8	0.2	1.2	1.5	5	5
実施例3	3	0.041	—	99.2	0.6	0.2	1.4	1.5	5	5
比較例1	4	0.039	0.032	74.8	25.0	0.2	1.0	5.5	10	55
比較例2	5	0.039	0.006	93.9	5.8	0.3	1.3	3.4	5	25

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【0071】

【表2】

	異方性 導電材料	接 触 抵 抗 (Ω)	
		初期	負荷後
実施例4	1	2.2	2.4
実施例5	2	2.3	2.5
実施例6	3	2.2	2.5
比較例3	4	1.8	8.2
比較例4	5	2.1	4.9

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【0072】

【発明の効果】

本発明により、導電被覆層である金属被覆層の耐腐食性が良好である導通安定性の優れた導電性微粒子を得ることができる。すなわち、本発明の導電性微粒子を用いて異方性導電材料を作成した場合、長期間の使用においても金属メッキ層の腐食やメッキ割れによる導電性低下を来さない経時安定性の高い電子材料を得ることができる。

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(54) CONDUCTIVE FINE PARTICLE AND ANISOTROPIC CONDUCTIVE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a conductive fine particle having a good corrosion resistance and stability with time of a metal coating layer, and an anisotropic conductive material using above.

SOLUTION: The resin fine particle is directly covered with a metal conductive layer made of gold having a purity of not less than 95 wt.%.

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CLAIMS

[Claim(s)]

[Claim 1]

The conductive particle which is a conductive particle which comes to form a metallic-coating layer in the front face of a resin particle directly, and is characterized by 95% of the weight or more of a metallic-coating layer consisting of gold.

[Claim 2]

The conductive particle according to claim 1 characterized by nickel contained in this metallic-coating layer being less than 5 % of the weight.

[Claim 3]

The conductive particle which is a conductive particle which comes to form a metallic-coating layer in the front face of a resin particle, and is characterized by ** which comes to form a metallic-coating layer by non-electrolyzed gold plate, and this 95% of the weight or more of metallic-coating layer consisting of gold after making the metal which has hydrogen absorption ability in this resin particle adsorb.

[Claim 4]

The conductive particle which is a conductive particle which comes to form a metallic-coating layer in the front face of a resin particle, and is characterized by nickel being less than 5 % of the weight by permuting nickel by gold nearly thoroughly by permutation gold plate, coming to form a metallic-coating layer, and this 95% of the weight or more of metallic-coating layer consisting of gold after preparing the metallic-coating layer by electroless nickel plating in this resin particle.

[Claim 5]

The conductive particle according to claim 4 characterized by being the conductive particle which comes to form a metallic-coating layer by non-electrolyzed gold plate further, for this 95% of the weight or more of metallic-coating layer being gold, and nickel being less than 5 % of the weight after permutation gold plate.

[Claim 6]

The conductive particle according to claim 1 to 5 characterized by for the mean particle diameter of a resin particle being 1-20 micrometers, and for coefficient of variation being 10% or less, and the thickness of a metallic-coating layer being 0.005-1 micrometer.

[Claim 7]

The anisotropy electrical conducting material characterized by using the conductive particle of a publication and growing into any 1 term of claims 1-6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

This invention relates to the conductive particle excellent in the corrosion resistance of a metallic-coating layer, and stability with the passage of time, and the anisotropy electrical conducting material using it.

[0001]

[Description of the Prior Art]

A conductive particle makes it mix with binder resin etc., and is widely used as a main component of anisotropy electrical conducting materials, such as an anisotropic conductive film, a conductive paste, electroconductive glue, and conductive adhesion material. In electronic equipment, such as a liquid crystal display device, a personal computer, and a cellular phone, these electrical conducting materials are used, putting between the substrates and electrode terminals which carry out phase opposite, in order to connect substrates electrically or to paste up small components, such as a semiconductor device, on a substrate electrically.

[0002]

A specific gravity be large, although metal particles, such as gold, silver, and nickel (it express Following nickel), had been conventionally used as this conductive particle, it be difficult to hold substrates for it at fixed spacing, since a configuration be also an infinite form, or it tended to exist in an uniformity in binder resin, the problem which make conductivity produce nonuniformity arose, and an activity be become difficult at the electronic parts to which fine pitch-ization progress every day.

Moreover, since the degree of hardness was high and lacking in resiliency, breakage was done to the substrate, and since the difference in coefficient of thermal expansion with binder resin was still greater, there was a case where might produce a crack in a connection by the abrupt change of temperature etc., and the defect of conductivity was caused with time in a long-term activity.

[0003]

For this reason, in recent years, particle size is uniform instead of metal particles, and the conductive particle which performed non-electrolyzed nickel plating has been widely used for the front face of non-conductive particles, such as a plastic bowl which has moderate reinforcement. However, nickel deteriorated, when contact resistance was high and the long duration pan was carried out to the bottom of high-humidity/temperature, and it had the fault of worsening contact conductivity further.

[0004]

In order to solve such a problem, non-electrolyzed nickel plating is performed to JP.7-118856.A on the surface of a spherical particle, and the conductive particle which made the permutation gold plate layer form in the upper layer further is indicated. However, generally it was difficult for nickel layer of a substrate to tend to make an oxide skin easily, and to make a golden coat into homogeneity for this effect. Furthermore, when partial exposure of a minute pinhole and nickel existed, the so-called "local battery" was produced, elution of Substrate nickel was accelerated, and eluted nickel had the trouble of depositing on the front face of a metallic-coating layer as an

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particle which has the physical properties at the time of compression of the arbitration which was suitable for the electrical conducting material one sort or by carrying out a two or more sort polymerization in the various polymerization nature monomers which have an ethylene nature partial saturation radical can be designed and compounded.

[0010]

When carrying out the polymerization of the polymerization nature monomer which has an ethylene nature partial saturation radical for this resin particle and obtaining it, as a monomer which has the above-mentioned ethylene nature partial saturation radical There are a monomer of non-cross-linking and a monomer of cross-linking. As a monomer of non-cross-linking For example, styrene monomers, such as styrene and alpha methyl styrene, an acrylic acid (meta), Carboxyl group content monomers, such as a maleic acid and a maleic anhydride, methyl (meta) acrylate, Ethyl (meta) acrylate, propyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, Cetyl (meta) acrylate, stearyl (meta) acrylate, cyclohexyl (meta) acrylate, Allyl (meta) acrylate, such as isobornyl (meta) acrylate 2-hydroxyethyl (meta) acrylate, glycerol (meta) acrylate, Oxygen atom content (meta) acrylate, such as polyoxyethylene (meta) acrylate and glycidyl (meta) acrylate Nitro content monomers, such as (meta) acrylonitrile, the methyl vinyl ether, Vinyl ether, such as ethyl vinyl ether and propyl vinyl ether Acid vinyl ester, such as vinyl acetate, butanoic acid vinyl, lauric acid vinyl, and stearic acid vinyl Those halogen content monomers, such as unsaturated hydrocarbon [such as ethylene, a pro bilene, en isoprene, and a butadiene] and trifluoromethyl (meta) acrylate, pentafluoro ethyl (meta) acrylate, vinyl chloride, and vinyl fluoride and KURORU styrene, etc. are mentioned.

[0011]

As a monomer of cross-linking, for example Moreover, tetramethylolethane tetrapod (meta) acrylate, Tetra-methylol METANTORI (meta) acrylate, tetra-methylol METANJ (meta) acrylate, TORMECHI roll pro pantry (meta) acrylate, dipentaerythritol hexa (meta) acrylate, Dipentaerythritol PENTA (meta) acrylate, glycerol RUTORI (meta) acrylate, And GURISERORUJI (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, Polyfunctional (meta) acrylate, such as polypropylene GURIKORUJI (meta) acrylate a triaryl (ISO) SHIANU rate and triaryl trimellitate — and Silane content monomers, such as gamma-(meta) acryloxypropyltrimethoxysilane, such as a divinylbenzene, diallyl phthalate, diaryl acrylamide, and diaryl ether, trimethoxysilyl styrene, and vinyltrimethoxysilane, are mentioned.

[0012]

The resin particle of this invention can be obtained by carrying out a polymerization by the approach (JP.6-273774.A) of carrying out the suspension polymerization of the polymerization nature monomer which has an above-mentioned ethylene nature partial saturation radical the bottom of a well-known approach, for example, existence of a radical polymerization initiator, the approach (JP.1-81810.A) of making the seed particle child non-constructing a bridge swell a monomer, and carrying out a polymerization to him with a radical polymerization initiator, etc.

[0013]

Although especially these resin particles are not limited, and may be used independently or two or more sorts may be used together, in order to be used as an electrical conducting material, importance is attached to the physical properties at the time of compression of a resin particle.

[0014]

for example, the thing whose 10% K value used as an index of a mechanical strength is 1000-15000MPa — desirable — further — it is also 2000-10000MPa — although — it is more desirable.

[0015]

It is measured, when 10% K value is the smooth indenter end face which consists of a cylinder made from a diamond with a diameter of 50 micrometers and compresses the resin particle obtained using the minute compression test machine (Shimadzu PCT-200) based on the Patent Publication Heisei No. 503180 [six to] official report under conditions of 0.27g [second] compression velocity and the 10g of the maximum trial overloads, and K value can be calculated 10% from the following formula,
K= (3/root2) and F=5-3/2 and R=1/2

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oxide, and reducing contact conductivity on it remarkably. Moreover, the metallic-coating layer which deteriorated becomes easy to produce a plating crack and peeling, the crack was produced in the deposit also by a little impact and a little oscillation, and the corrosion and the plating crack of such a metal deposit could become the cause of it not only causing poor conductivity, but reducing the dependability of an electrical conducting material remarkably when corrosion advances with time, when it was used as an electrical conducting material.

[0005]

The approach of making gold JP.9-171714.A adhere to the front face of a resin particle with a dry type coating method, and on the other hand, covering gold with non-electrolyzed gold plate further is indicated. However, since it was difficult, it was not what is still enough satisfied to a demand of the further stability with the passage of time accompanying the rapid advance of electronic equipment in recent years to make gold adhere to a particle uniformly in dry type coating.

[0006]

[Problem(s) to be Solved by the Invention]

The place which this invention solves the above-mentioned trouble and is made into the object has the uniform metallic-coating layer which is an electric conduction enveloping layer, and its corrosion resistance is high, and it is to offer the conductive particle which was excellent in stability with the passage of time. Furthermore, it is in the thing which do not cause the conductive lowering by the corrosion or the plating crack of a metal deposit in a prolonged activity and for which it passes and the high anisotropy electrical conducting material of the Tokiyasu quality is offered by using this conductive layer.

[0007]

[Means for Solving the Problem]

As a result of this invention persons' inquiring wholeheartedly, it came to complete a header and this invention for the conductive particle which covered the resin particle with the metal conductive layer which purity becomes from 95% of the weight or more of gold having remarkably high corrosion resistance, and passing through it, without producing a local battery, and its Tokiyasu quality improving remarkably.

[0008]

The conductive particle of this invention is a conductive particle which comes to form a metallic-coating layer in the front face of a resin particle directly, and is characterized by 95% of the weight or more of a metallic-coating layer consisting of gold. A conductive particle.

Furthermore, after making the metal which has hydrogen absorption ability in a resin particle adsorb it is the conductive particle which comes to form a metallic-coating layer by non-electrolyzed gold plate. What is characterized by this 95% of the weight or more of metallic-coating layer consisting of gold. Moreover, after preparing the metallic-coating layer by electroless nickel plating in a resin particle, it is the conductive particle which comes to form a metallic-coating layer by permuting nickel by gold nearly thoroughly by permutation gold plate. What is characterized by for 95% of the weight or more of a metallic-coating layer being gold, and nickel being less than 5 % of the weight. And it is the conductive particle which comes to form a metallic-coating layer by non-electrolyzed gold plate further. It is what is characterized by for this 95% of the weight or more of metallic-coating layer being gold, and nickel being less than 5 % of the weight. These form the metallic-coating layer with it on the front face of a resin particle, and are constituted based on the result that it is what passes without producing a local battery and is excellent in the Tokiyasu quality. [high corrosion resistance and] [uniform]

[0009]

This invention is explained in full detail below.

As a resin particle of this invention, the various organic substance is suitable and acrylic resin, such as polyolefines, such as polyethylene, polypropylene, polystyrene, a polyvinyl chloride, a polyvinylidene chloride, polypropylene, a polyisobutylene, and polybutadiene, polymethylmethacrylate, and polymethyl acrylate, polyethylene terephthalate, polysulfone, a polycarbonate, a polyamide, phenol formaldehyde resin, melamine formaldehyde resin, benzoguanamine formaldehyde resins, formaldehyde resin, etc. are used. For example, the resin

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F: The load value in 10% compression set of a particle (kg)
S: The compression in 10% compression set of a particle — e variation rate (mm)
R: The radius of a particle (mm)

[0016]

Since less than 1000 are not enough as the reinforcement of a resin particle, when above-mentioned 10% K value carries out a compression set, destruction of a particle arises, and it stops achieving the function as an electrical conducting material. Conversely, since an electrode may be damaged when larger than 15000, it is not desirable.

[0017]

Furthermore, as for the resin particle of this invention, it is desirable that a recovery factor is 20% or more. A recovery factor is a recovery factor after carrying out the load of the load of 1gf to a particle, and is 40% or more more preferably. When a conductive particle is manufactured using the resin particle whose recovery factor is less than 20%, since it does not return even if it deforms, when it compresses, a faulty connection may be broken up.

[0018]

When carrying out the polymerization of the polymerization nature monomer which has the above-mentioned ethylene nature partial saturation radical for the resin particle used for this invention and obtaining it, considering these particle physical properties, it is more desirable as a constituent in a resin particle to contain a cross-linking monomer 20% of the weight or more more preferably at least 5% of the weight or more. It produces destruction or permanent deformation of a conductive particle and is not desirable, when above-mentioned 10% K value and a recovery factor fall that a cross-linking monomer is less than 5 % of the weight and sticking-by-pressure processing is performed.

[0019]

The conductive particle of this invention is obtained by forming in the front face of the above-mentioned resin particle directly the metallic-coating layer which purity becomes from 95% of the weight or more of gold. In this case, forming in a resin particle directly means that the substrate layer by no electrolyzing [nickel] etc. does not exist between the metallic-coating layers and resin particles which purity becomes from 95% of the weight or more of gold. Moreover, although it is desirable to cover all resin particles to homogeneity, even if this metallic-coating layer has the pinhole and coat nonuniformity of extent which has effect neither in conductivity nor plating exfoliation, carry out another level difference, support and there is. [no] Because, even if there are a minute pinhole and slight coat nonuniformity, since the substrate nickel layer which should serve as a radii point of a local battery does not fully exist, the corrosion or deterioration with time of a metal conductive layer are not caused.

[0020]

The approach of listing to below as the formation approach of this metallic-coating layer is suitable.

1. How to Form Gold in Front Face of Resin Particle Directly by Electroless Deposition, after Making Metal Which Has Hydrogen Absorption Ability in Resin Particle Adsorb
2. How to Give Non-Electrolyzed Nickel Deposit to Front Face of Resin Particle, and Permute Nearly Thoroughly by Gold after That

How to make the thickness of a golden enveloping layer increase to the metallic-coating layer which **ed) by 3.2 by electroplating or electroless deposition further.

[0021]

Although the non-electrolyzed gold plate reagent of the self-reduction type with which versatility is marketed can also be used as the approach of 1 and it is not limited especially, generally it consists of the electroless deposition process the etching process and catalyst chemically-modified degree.

[0022]

An etching process is a process for making minute irregularity form in the front face of a base material particle using strong-base solutions, such as strong acid, such as oxidizers, such as chromic acid and sulfuric acid-chromic acid mixture and a permanganic acid solution, and a hydrochloric acid, a sulfuric acid, a sodium hydroxide, and a potassium hydroxide, etc., and

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improving adhesion of a deposit by this.

[0023]

A catalyst chemically-modified degree is a process in which the catalyst bed which becomes by making a resin particle carry out adsorption generation of the metal which has the hydrogen absorption ability which can serve as an origin of the electrolytic deposition of degree process on the front face of a resin particle is made to form. Although are not limited especially as a metal which has hydrogen absorption ability here, and Pd, Pt, Au, nickel, etc. are mentioned, it is simplest to use Pd to which the commercial reagent etc. has appeared on the market widely, and it is desirable. The others in the case of not being limited and using commercial Pd catalyst-sized liquid etc. especially as a catalyst chemically-modified [using Pd] degree. For example, after the resin particle etched into the solution which consists of a palladium chloride and tin chloride is immersed, how for it to be activated with alkali solutions, such as acids, such as a sulfuric acid and a hydrochloric acid, and a sodium hydroxide, and to deposit Pd on a resin particle front face. After the resin particle etched into the sulfuric-acid palladium solution is immersed, the method of being activated with the solution containing reducing agents, such as dimethylamine borane, and depositing Pd on a resin particle front face etc. is mentioned. However, the latter approach of the former is [that tin and a chloride remain in a metal coat in many cases] more more desirable.

[0024]

An electroless deposition process is performed by immersing the resin particle which gave the catalyst into the solution which contains gold under existence of a reducing agent, and depositing gold on the front face of a resin particle with the given catalyst as the starting point.

[0025]

In this case, it is not limited especially as a reducing agent used, and boron compounds, such as tetrahydroborate, cyano tetrahydroborate, dimethylamine borane, and hydrazine borane, hypophosphite, a hydrazine, grape sugar, formalin, an ascorbic acid, a titanium trichloride, etc. can be used. Moreover, it is suitable to usually use golden content water solubility salts, such as a gold cyanide salt, a 2 gold-cyanide salt, and a gold salt etc. tetrachloride, as an approach of making gold containing in a solution.

[0026]

These reducing agents and a golden content water solubility salt can be dissolved with additives and stabilizers, such as chelating agents, such as citrate and an ethylenediaminetetraacetic acid salt, a potassium cyanide, a sodium cyanide, triethanolamine, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, polyethyleneimine, and lead acetate, the initial make-up of electrolytic bath of the self-reduction type radio solution gold plate bath can be carried out, and a golden enveloping layer can be directly formed in the front face of a resin particle using these plating baths.

[0027]

Although other metals which carry out the eutectoid of the metallic-coating layer of this invention with gold although gold serves as a principal component may be contained, for example, Co, Cu, Zn, Fe, Mn, Cr, V, Mo, Pd, Sn, nickel, etc. may be contained in the electric conduction enveloping layer with gold, as for golden purity, it is desirable that it is more than 95 W/W%, and it is more than 98 W/W% more preferably. It falls [the flexibility of a contact conductivity metallurgy group coat] that golden purity is less than [95 W/W%] and is not desirable.

[0028]

By the approach of 1, the thickness of a metallic-coating layer is controllable by the amount of reagents of permutation gold plate, time amount, temperature, etc. to arbitration.

[0029]

Although the approach of 2 is an approach of forming nickel metal layer, supplying this to a permutation gold plate bath, and making nickel once permutes by gold nearly thoroughly by electroless nickel plating and is not limited especially, it consists of non-electrolyzed nickel plating process and the permutation gold plate process the etching process and catalyst chemically-modified degree similarly. Although the etching process and catalyst chemically-modified degree is the same as that of the approach of one and non-electrolyzed nickel plating

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The resin particle of this invention has that desirable whose mean particle diameter is 0.5-100 micrometers, and what is the range which is 1-20 micrometers is more desirable. When a resin particle is less than 0.5 micrometers, in case a conductive enveloping layer is formed, it is easy to produce condensation, and the problem that the conductive particle manufactured using this particle causes a contiguity inter-electrode short circuit may be generated. When the mean particle diameter of a resin particle exceeds 100 micrometers, the problem that the conductive enveloping layer of the conductive particle manufactured using this particle becomes easy to separate, and dependability falls may occur.

[0030]

Moreover, that whose coefficient of variation obtained by σ/μ (mg) standard deviation obtained from particle size distribution with mean particle diameter is 10% or less is more desirable. Moreover, if a conductive particle is manufactured using the resin particle to which coefficient of variation exceeds 10%, it will become difficult to control to arbitration the electrode spacing which carries out phase opposite.

[0031]

It is used, in case the conductive particle of this invention is used as a main component of various anisotropy electrical conducting materials and two substrates and electrode terminals which carry out phase opposite are connected electrically, and the anisotropy electrical conducting material containing the conductive particle of this invention is also contained in this invention. It is not limited especially as that approach, for example, a conductive particle is distributed in binder resin, it considers as anisotropy electric conduction adhesives, and the approach of connecting using these anisotropy electric conduction adhesives, the approach of connecting using a binder and a conductive particle independently, etc. are mentioned.

[0032]

As the above-mentioned anisotropy electric conduction adhesives, especially if a conductive particle is distributed in insulating binder resin, it will not be limited, but the anisotropy electric conduction film, anisotropy conductive paste, anisotropy electric conduction ink, etc. are included.

[0033]

The constituent hardened with light and heat, such as a hardenability resin constituent obtained by the reaction with curing agents, such as a monomer which is not limited especially as this binder resin, for example, has thermoplastics, such as acrylate resin, ethylene-vinyl acetate resin, and a styrene butadiene block copolymer, and a glycidyl group, and oligomer, isocyanate, is mentioned. As for the coating thickness of the above-mentioned anisotropy electrical conducting material, it is desirable that calculate from the mean particle diameter of a conductive particle and the specification of a connection electrode which were used, a conductive particle is pinched by connection inter-electrode, and between junction substrates is fully made to be fitted with a glue line.

[0040]

The anisotropy electric conduction film adds a solvent to for example, the above-mentioned anisotropy electric conduction adhesives, makes it the shape of a solution, can cast this solution on a mold releasing film, can make a coat, and can roll round and make on a roll what evaporated the solvent from a coat. It can place on the electrode on which it is beginning to wind a coat around with a mold releasing film in the case of an activity, and a coat should be pasted up, and can be made to connect by carrying out heating compression of the counterelectrode in piles on this.

[0041]

Anisotropy conductive paste is obtained by making for example, anisotropy electric conduction adhesives into the shape of a paste, puts this into a suitable dispenser, applies it to the thickness of a request on the electrode which should be connected, and on this, it can connect a counterelectrode superposition and by pressurizing and stiffening resin while heating.

[0042]

Anisotropy electric conduction ink can be obtained by giving the viscosity which added the solvent to for example, the above-mentioned anisotropy electric conduction adhesives, and was

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bath by which versatility is marketed also about non-electrolyzed nickel plating process can be used. For example, it is carried out by immersing the resin particle which gave the catalyst into the solution which contains nickel salt under existence of reducing agents, such as hypophosphorous acid and dimethylamine borane, and depositing nickel on the front face of a resin particle with the given catalyst as the starting point. Although a permutation gold plate process is a process permuted by nickel and gold using the difference in the ionization tendency of nickel and gold and the permutation gold plate bath by which versatility is marketed can be used, the initial make-up of electrolytic bath of the golden content water solubility salts, such as chelating agents, such as citrate and an ethylenediaminetetraacetic acid salt, a gold cyanide salt, a 2 gold-cyanide salt, and a gold salt etc. tetrachloride, can be dissolved and carried out, for example. Usually, the reducing agent is not contained in this permutation gold plate bath.

[0030]

Although the approach of 2 has the advantage that non-electrolyzed nickel plating bath more stable than the non-electrolyzed gold plate bath used by the approach of 1 can be used, it is necessary to make nickel permute by gold nearly thoroughly in a permutation gold plate process. It is desirable that a golden substitutional rate is 95 % of the weight or more as golden purity in a metallic-coating layer in this case as it is nearly perfect, and it is 98 % of the weight or more more preferably. It falls [the flexibility of a contact conductivity metallurgy group coat] that golden purity is 95 or less % of the weight and is not desirable.

[0031]

Moreover, it is desirable that nickel which remains is less than 5 % of the weight, and permuting with gold is more desirable until nickel becomes 2 or less % of the weight. The survival rate of nickel becomes easy to produce a local battery to be 5 % of the weight or more with a minute pinhole or coat nonuniformity as the starting point and is not desirable.

[0032]

Although it depends for the thickness of a metallic-coating layer on the thickness of non-electrolyzed nickel layer by the approach of 2, in order to gather a golden substitutional rate, non-electrolyzed nickel deposit should not be made not much thick, but it is more desirable that it is 0.04 micrometers or less as for non-electrolyzed nickel deposit, and it is 0.02 micrometers or less by the approach of 2. If nickel deposit exceeds 0.04 micrometers, 95% of the weight or more of a golden permutation will become difficult. In order to be unable to make a gold plate layer not much thick by the approach of 2 by such reason but to make the thickness of a golden enveloping layer increase further, it is more desirable to use the approach of 3.

[0033]

Since non-electrolyzed nickel deposit can be set up by the approach of 3 beforehand more thinly than the approach of 2, it becomes possible to make the survival rate of nickel lower. The approach of non-electrolyzed gold plate used by the approach of 3 is made like the approach of 1. As for the content of the gold in the metallic-coating layer obtained eventually, it is desirable that it is 95 % of the weight or more, and it is 98 % of the weight or more more preferably. It falls [the flexibility of a contact conductivity metallurgy group coat] that golden purity is 95 or less % of the weight and is not desirable.

Moreover, it is desirable that nickel which remains is less than 5 % of the weight, and permuting with gold is more desirable until nickel becomes 2 or less % of the weight. The survival rate of nickel becomes easy to produce a local battery to be 5 % of the weight or more with a minute pinhole or coat nonuniformity as the starting point and is not desirable.

[0034]

Although it changes also with mean particle diameter of the resin particle covered as thickness of this metallic-coating layer, it is desirable that it is 0.005-1 micrometer, and it is more desirable that it is further 0.01-0.3 micrometers. Sufficient effectiveness as an electric conduction enveloping layer is not acquired as the thickness of this enveloping layer is less than 0.005 micrometers, and it is not desirable. Moreover, since it becomes large too much, or the grain child specific gravity for which this enveloping layer exceeds 1 micrometer needs expensive gold for a large quantity and serves as the cost high, it is not so desirable.

[0035]

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suitable for printing, can be screen-stenciled on the electrode on which this should be pasted up, can evaporate a solvent after that, and can be connected by carrying out heating compression of the counterelectrode in piles on this.

[0043]

[Function]

The conductive particle obtained by this invention has the uniform metallic-coating layer which is an electric conduction enveloping layer, and can obtain the conductive particle which was excellent in stability with the passage of time with good corrosion resistance. Furthermore, by using this conductive particle, it can cause and pass through the conductive lowering by the corrosion and the plating crack of a metal deposit also in a prolonged activity, and the high anisotropy electrical conducting material of the Tokiyasu quality can be obtained.

[0044]

[Example]

Although an example is raised to below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0045]

[Example 1]

The mixed liquor of the divinylbenzene 80 section, the TORIMECHI roll pro pantry (meta) acrylate 20 section, and the benzoyl-peroxide 2 section was added to the 3% water-solution 800 of polyvinyl alcohol (Nippon Synthetic Chemical Industry make GH-20) section (following weight section), it agitated with the homogenizer, and grain refining was performed. Temperature up was carried out to 80 degrees C under the nitrogen air current, agitating after that, and the reaction was performed for 15 hours. The resin particle which performs classification actuation after washing with distilled water and a methanol, and serves as mean-particle-diameter =5.3micrometer and a core material of 50% of coefficient of variation in the obtained particle was obtained. When 10% K value of this resin particle was measured by the above-mentioned approach, 4100MPa and a recovery factor were 51%. The pre DIP liquid for powder plating (the Okuno Pharmaceuticals company make) was made to distribute 10g of this resin particle, and it etched by stirring for 30 minutes at 30 degrees C.

[0046]

Then, rinsed this particle, added in 100ml of Pd catalyst-sized liquid which contains sulfuric-acid palladium 1% of the weight, it was made to stir for 30 minutes at 30 degrees C, and palladium ion was made to stick to a particle. After separating and rinsing this particle, it added in 0.5% of the weight of dimethylamine borane liquid (it adjusts to pH8.0), and the resin particle which activated Pd was obtained.

[0047]

After adding 1000ml (SERAGORUDO 6020, product made from EEJA) of reduction type radio solution liquid gilding which carries out 7 g/L content of the 2 gold-cyanide potassium to this resin particle and making it fully distribute using an ultrasonic washing machine, non-electrolyzed gold plate was carried out adding a water solution gradually 10%, when carrying out temperature up to 70 degrees C, stirring. When the golden enveloping layer was about set to 0.04 micrometers, the stop and the particle were separated for the reaction. With distilled water, it fully rinsed, an after alcoholic permutation is carried out, the vacuum drying of this particle was carried out, and the conductive particle 1 was obtained. When this conductive particle 1 was observed in 5000 times using the electron microscope (SEM), it has checked that the uniform metallic-coating layer without a plating deficit etc. was formed.

Moreover, thickness measurement of the metallic-coating layer listed to below about the obtained conductive particle 1, a metal content ratio measurement, measurement of conductivity and the adhesion of an electric conduction enveloping layer, the conductivity behind a high-humidity/temperature load, etc. measured change, and the result was shown in a table 1.

[0048]

(Thickness measurement of a metallic-coating layer)

0.5g of conductive particles 1 is weighed precisely, after dissolving a metallic-coating layer thoroughly in addition to the mixed liquor which consists of 5ml of nitric acids, and 10ml of 37%

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hydrochloric acids 60%, 20ml of saturated water solutions of hydrazine sulfate was added, it heated at 80 degrees C for 1 hour, and gold was settled. The solution containing this precipitating gold was separated through the filter paper, and it put into the crucible with the filter paper, it destroyed by fire at 900 degrees for 2 hours, and gold was collected. The weight of the collected gold was measured and golden content (it is called WAU) was computed. Golden deposit thickness was computed by the following formula from the obtained golden content. Gold plate thickness (micrometer) = (rhoPxWAUxD) / (6xrhoAUx (100-WAU))

rhoP: The specific gravity of a resin particle, the specific gravity of rhoAU:gold, WAU:golden (%) and content, D: Mean particle diameter of a resin particle (micrometer)

[0049]

(Metal content ratio measurement of a metallic-coating layer)

The solution which dissolved the metallic-coating layer thoroughly like thickness measurement of the above-mentioned metallic-coating layer was measured with the ICP AEM plan, and weight % of metals contained in addition to this, such as gold and nickel, was computed.

[0050]

(Measurement of conductivity and the adhesion of an electric conduction enveloping layer)

The contact resistance value in the event of compressing the conductive particle 1 using a minute compression electric resistance measuring instrument (PCT-200 **, Shimadzu Corp. make), and particle size being compressed 20% was measured. This measurement was carried out to 20 particles and that average was calculated.

[0051]

Moreover, when it compressed gradually to 50% of mean particle diameter succeeding, the particle to which resistance increases to 10ohms or more suddenly in the process was accepted. When these particles were observed with the optical microscope, exfoliation of an electric conduction enveloping layer and destruction had occurred, and it asked for the generating ratio of these particles as a conductive destructive ratio. It is shown that there are so few plating cracks that this conductive destructive ratio is low.

[0052]

(Measurement of change, such as conductivity behind a high-humidity/temperature load)

After leaving the conductive particle 1 for 20 days under 85 degrees C and the ambient atmosphere of 95% of relative humidity, it asked for the contact resistance value and the conductive destructive ratio behind a load like the above-mentioned conductive measurement. It is shown that it is the conductive particle excellent in stability with the passage of time, so that the difference of the measured value before and behind a load is small.

[0053]

(Example 2)

500ml of distilled water was added to the resin particle which was obtained like the example 1 and which activated Pd, and particle suspension was obtained by making it fully distribute using a sonication machine. Stirring this suspension at 50 degrees C, the electroless deposition liquid (pH is adjusted to 7.5) which consists of nickel-sulfate (six hydrates) 50 g/L, dimethylamine borane 5 g/L, and citric-acid 50g/L was added gradually, and electroless nickel plating was performed. When this enveloping layer was set to about 0.02 micrometers, addition of electroless deposition liquid was stopped, and the particle was separated. After fully rinsing this particle with distilled water, it was made to react at 70 degrees C for 60 minutes, adding and stirring to 2000ml (Japanese high grade chemistry company make, IM-GoldST) of permutation liquid gilding containing NISHIAN-ized golden potassium 7g, and gold permuted nickel deposit thoroughly. After reaction termination, the alcoholic permutation was separated, rinsed and carried out, the after vacuum drying of the particle was carried out, and the conductive particle 2 was obtained.

[0054]

When this conductive particle 2 was observed in SEM like the example 1, it has checked that the uniform metallic-coating layer without a plating deficit etc. was formed. Thickness measurement of a metallic-coating layer, a metal content ratio measurement, measurement of conductivity and the adhesion of an electric conduction enveloping layer, the conductivity behind a high-humidity/temperature load, etc. measured change for the conductive particle 2 like the example

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Gold plate thickness (micrometer) = (rhoPxWAUxD) / (6xrhoAUx (100-WAU-WNi))
nickel deposit thickness (micrometer) = (rhoPxWNiND) / (6xrhonickelx (100-WAU-WNi))
rhoP: Specific gravity of a resin particle, rhoAU: Golden specific gravity Specific gravity of rhonickel:nickel layer.

WAU: Golden content (%) WNi:nickel (%) and content, and D: Mean particle diameter of a resin particle (micrometer)

[0062]

From a table 1, the conductive particles 1-3 obtained in the examples 1-3 are understood that there are few conductive change after a load and increments in a plating crack, and the corrosion resistance of a metallic-coating layer is high compared with the conductive particles 4 and 5 obtained in the examples 1 and 2 of a comparison. Although a big change was not accepted in the front-face nature by the conductive particles 1-3 when the conductive particle 4 behind a load was dark-color-ized compared with other conductive particles and the conductive particle before and behind each load was observed in 5000 times using the electron microscope (SEM), surface deterioration of the shape of a blow hole of ** was accepted by the conductive particles 4 and 5 of the example of a comparison. Since this was easily dissolved in dilute hydrochloric acid and nickel was detected from this solution, nickel of a lower layer [the effect of a local battery being generated etc.] is eluted, and this surface deterioration is considered to have become nickel oxide etc. and to have adhered to the front face of a conductive particle.

[0063]

(Example 4)

Mixed the conductive particle 1 at 5 W/W% of a rate in epoxy system adhesives (Furukawa chemically-modified company make, SE-4500), the homogenizer was made to fully distribute, and the anisotropy electric conduction adhesives 1 were produced.

[0064]

These anisotropy electric conduction adhesives were applied, respectively on the glass substrate with which the ITO electrode was formed by width of face of 300 micrometers, and the glass substrate same from this was piled up so that an ITO electrode might become a cross. After heating for 30 minutes and carrying out sticking-by-pressure hardening at 160 degrees C, applying the pressure of 30kg/cm2 to this, the contact resistance value was measured by 4 terminal method about the conductive particle 1 which exists in the part which ITO intersects. Counting of the number of the conductive particles 1 which exist in the crossing part was carried out with the optical microscope, the acquired contact resistance value was ** (ed) by this number, and it considered as the contact resistance value per conductive particle.

[0065]

After leaving this substrate for 20 days furthermore under 85 degrees C and the ambient atmosphere of 95% of relative humidity, same measurement was carried out again. This measurement was carried out n= 5 times, respectively, and the average was shown in a table 2. It is shown that conductive stability with the passage of time is good, so that this contact resistance value change is small.

[0066]

(Example 5)

Except having used the conductive particle 2, the same actuation as an example 4 was performed, the anisotropy electric conduction adhesives 2 were produced, and the same measurement as an example 4 was carried out. The obtained result was shown in a table 2.

(Example 6)

Except having used the conductive particle 3, the same actuation as an example 4 was performed, the anisotropy electric conduction adhesives 3 were produced, and the same measurement as an example 4 was carried out. The obtained result was shown in a table 2.

[0067]

(Example 3 of a comparison)

Except having used the conductive particle 4, the same actuation as an example 4 was performed, the anisotropy electric conduction adhesives 4 were produced, and the same

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1, and the result was shown in a table 1.

[0055]

(Example 3)

Electroless nickel plating was performed like the example 2, when this nickel enveloping layer was set to about 0.01 micrometers, addition of electroless deposition liquid was stopped, and the particle was separated. Gold permuted nickel deposit for this particle thoroughly like the example 2. Self-reduction type radio solution gold plate was again performed like the example 1, after reaction termination, the particle was separated, it rinsed, the alcoholic permutation was carried out, the after vacuum drying of the obtained particle was carried out, and the conductive particle 3 was obtained. When this conductive particle 3 was observed in SEM like the example 1, it has checked that the uniform metallic-coating layer without a plating deficit etc. was formed.

[0056]

Thickness measurement of a metallic-coating layer, a metal content ratio measurement, measurement of conductivity and the adhesion of an electric conduction enveloping layer, the conductivity behind a high-humidity/temperature load, etc. measured change for the conductive particle 3 like the example 1, and the result was shown in a table 1.

[0057]

(Example 1 of a comparison)

Electroless nickel plating was performed like the example 2, when this nickel enveloping layer was set to about 0.05 micrometers, addition of electroless deposition liquid was stopped, and the particle was separated. After fully rinsing this particle with distilled water, the reaction was stopped, when it was made to react at 70 degrees C and the thickness of a permutation gold plate layer became about 400A, adding and stirring to 2000ml (Japanese high grade chemistry company make, IM-GoldST) of permutation liquid gilding containing gold cyanide potassium 5g. After that, the alcoholic permutation was separated, rinsed and carried out, the after vacuum drying of the particle was carried out, and the conductive particle 4 was obtained.

[0058]

Like [particle / 4 / conductive] the example 1, conductivity, measurement of the adhesion of an electric conduction enveloping layer, the conductivity behind a high-humidity/temperature load, etc. measured change, and the result was shown in a table 1.

[0059]

(Example 2 of a comparison)

In the example 2, except having reduced the reaction time of permutation gold plate from 60 minutes in 10 minutes, and having made the substitutional rate to gold into imperfection, it carried out similarly and the conductive particle 5 was obtained. Like [particle / 5 / which was obtained / conductive] the example 1, conductivity, measurement of the adhesion of an electric conduction enveloping layer, the conductivity behind a high-humidity/temperature load, etc. measured change, and the result was shown in a table 1.

[0060]

In addition, the gold and nickel thickness of the conductive particles 4 and 5 were measured by the following approaches. (Measurement of gold and nickel thickness)

0.5g of conductive particles is weighed precisely, after dissolving a metallic-coating layer thoroughly in addition to the mixed liquor which consists of 5ml of nitric acids, and 10ml of 37% hydrochloric acids 60%, 20ml of saturated water solutions of hydrazine sulfate was added, it heated at 80 degrees C for 1 hour, and gold was settled. The solution containing this precipitating gold was separated through the filter paper, and it put into the crucible with the filter paper, it destroyed by fire at 900 degrees for 2 hours, and gold was collected. The weight of the collected gold was measured and the golden content WAU was computed. Moreover, filtrate carried out the scalpel rise at accuracy at 200ml, and measured nickel content (it is called WNi) with the EDTA standard solution of 0.01 mol/L by using bottom Cu-PAN of the ascensece as an indicator.

[0061]

The deposit thickness of gold and nickel was computed by the following formula from the golden content and nickel content which were obtained.

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measurement as an example 4 was carried out. The obtained result was shown in a table 2.

[0068]

(Example 4 of a comparison)

Except having used the conductive particle 5, the same actuation as an example 4 was performed, the anisotropy electric conduction adhesives 5 were produced, and the same measurement as an example 4 was carried out. The obtained result was shown in a table 2.

[0069]

A table 2 shows that pass through the anisotropy electric conduction adhesives 1-3 which ** (ed) in the examples 4-6 rather than the anisotropy electric conduction adhesives 4 and 5 of the examples 3 and 4 of a comparison, and the Tokiyasu quality is excellent.

[0070]

(A table 1)

	導電性 炭粒子 (μm)	Au厚 (μm)	Ni厚 (μm)	被覆層の含有率 (%)			接点抵抗 (Ω)				導電性破壊比 (%)			
				Au	Ni	その他 (Pd)	初期	負荷後	初期	負荷後	初期	負荷後	初期	負荷後
実施例 1	1	0.040	—	99.7	0.0	0.3	1.2	1.3	—	—	0	0	—	—
実施例 2	2	0.040	—	98.1	1.8	0.2	1.2	1.5	—	—	5	5	—	—
実施例 3	3	0.041	—	99.2	0.6	0.2	1.4	1.5	—	—	5	5	—	—
比較例 1	4	0.039	0.032	74.8	25.0	0.2	1.0	5.5	10	55	—	—	—	—
比較例 2	5	0.039	0.006	93.9	5.8	0.3	1.3	3.4	5	25	—	—	—	—

[0071]

(A table 2)

	異方性 導電材料	接点抵抗 (Ω)	
		初期	負荷後
実施例 4	1	2.2	2.4
実施例 5	2	2.3	2.5
実施例 6	3	2.2	2.5
比較例 3	4	1.8	8.2
比較例 4	5	2.1	4.9

[0072]

(Effect of the Invention)

By this invention, the corrosion resistance of the metallic-coating layer which is an electric conduction enveloping layer can obtain the conductive particle which was excellent in good flow

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stability. That is, when an anisotropy electrical conducting material is created using the conductive particle of this invention, it can cause and pass through the conductive lowering by the corrosion and the plating crack of a metal deposit also in a prolonged activity, and the high electronic ingredient of the Tokiyasu quality can be obtained.

[Translation done.]

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